[Detailed Description of the Invention]

Technical field This invention relates to the manufacture method of a lithium battery and a lithium secondary battery using the electrode material and the electrode which are obtained by the manufacture method of the electrode material for lithium batteries, and the electrode for lithium batteries, and this manufacture method.

Background art The battery characteristics, such as charge and discharge voltage, the charge-and-discharge cycle length characteristic, and the preservation characteristic, are greatly influenced in recent years with the electrode with which the lithium secondary battery with which research and development are done briskly is used. From this, improvement in the battery characteristic is achieved by improving an electrode active material.

When lithium metal was used as a **** active material, per weight and per volume could constitute the battery of high energy density, but in negative best quality, lithium deposited in the shape of a DENDO light at the time of charge, and there was a problem of causing an internal short circuit.

On the other hand, the lithium secondary battery using lithium, aluminum, silicon, tin, etc. alloy etc. as an electrode is electrochemically reported in the case of charge (Solid State Ionics, 113-115, p57 (1998)). The various rechargeable batteries which especially silicon has large theoretical capacity, are promising as **** for batteries which shows high capacity, and make this **** are proposed among these (JP H10-255768,A). However, sufficient cycle characteristic is not acquired from the alloy itself which is an electrode active material fine-powdering this kind of alloy **** by charge and discharge, and the current collection characteristic getting worse.

Indication of invention The purpose of this invention is to offer the manufacture method of a lithium battery and a lithium secondary battery using the electrode material and the electrode which are obtained by the manufacture method of a new electrode material for lithium batteries, and the electrode for lithium batteries, and this manufacture method.

Hereafter, although invention of a description is explained to each claim, the matter common to two or more claims is explained as "this invention."

The 1st aspect of affairs of this invention is the manufacture method of the electrode material for lithium batteries characterized by making amorphous silicon thin films, such as a micro crystalline silicon thin film, deposit on a substrate, and using amorphous silicon thin films, such as this micro crystalline silicon thin film, as an active material.

Generally silicon is divided roughly into amorphous silicon and micro crystalline silicon, polycrystalline silicon, and single crystal silicon by crystalline difference. The "amorphous silicon" in this invention is silicon of the structure which amorphous silicon and micro crystalline silicon excluding polycrystalline silicon and single crystal silicon are meant, and there is no long range order of nm order, and has the short range order below mum order. In the Raman

spectroscopic analysis which amorphous silicon mentions later, about [520cm-1] one peak corresponding to a crystalline region is not detected substantially. Both about [520cm-1] one peak on the Raman spectroscopic analysis and corresponding to a crystalline region in micro crystallite silicon and about [480cm-1] one peak corresponding to an amorphous field are detected substantially. Therefore, micro crystallite silicon consists of a crystalline region and an amorphous field substantially. About [480cm-1] one peak on the Raman spectroscopic analysis and corresponding to an amorphous field in polycrystalline silicon and single crystal silicon is not detected substantially.
As for the size of the crystalline region in a micro crystallite silicon thin film, in this invention, it is desirable that it is 0.5nm or more as a diameter of a crystal grain computed from the formula of an X diffraction spectrum and Scherrer.
The method of computing the diameter of a crystal grain from the formula of an X diffraction spectrum and Scherrer is indicated to the 375th page of the thin film handbook (the volume 1st edition and on 131st committee of the Japan Society for the Promotion of Science thin film, Ohm-Sha issue).
As the above-mentioned diameter of a crystal grain, it is 1nm or more that it is 0.5nm or more as mentioned above desirable still more preferably. The crystalline region where each atom aligned in the direction of a one plane regularly as a crystalline region of the minimum size in the field of the three dimensions used as the size of about three atoms, i.e., the field of the three dimensions which consist of about 27 atoms, is illustrated.
The diameter of a crystal grain of the diameter of a crystal grain observed, for example with a transmission electron microscope computed from the formula of the above-mentioned X diffraction spectrum and Scherrer does not necessarily correspond. Moreover, you may be the crystalline region which extended for a long time in the specific direction, for example, the thickness direction. The length of the thickness direction in this case may be about 10 micrometers.
In this invention, it is desirable that about [480cm-1] one peak intensity ratio (about [480cm-1] and about [520cm-1]) to about [520cm-1] one peak intensity in the Raman spectroscopic analysis of a micro crystallite silicon thin film is 0.05 or more.
The above-mentioned peak intensity ratio is 0.1 or more still more preferably. The upper limit in particular of the above-mentioned peak intensity ratio is not set up, and about [480cm-1] one peak corresponding to an amorphous field should just be detected substantially. In addition, shifting about [480cm-1] one peak corresponding to an amorphous field about [10cm-1] one is known. Moreover, shifting about [520cm-1] one peak corresponding to a crystalline region about [5cm-1] one is known. In addition, since about [480cm-1] one peak is a broadcloth peak, the skirt of a peak may spread to about [520cm-1] one. In this case, the above-mentioned peak intensity ratio is computed by making the height of about [520cm-1] one peak into peak

intensity, without deducting the spread portion of a peak.
In this invention, a CVD method, the sputtering method, a thermal-spraying method, or a vacuum deposition method is mentioned as a method of depositing an amorphous silicon thin film.
One of the concrete manufacture methods according to the 1st aspect of affairs supplies the materials powder containing the material gas or the silicon atom which contains a silicon atom from the gaseous phase, it makes an amorphous silicon thin film deposit on a substrate, and is characterized by using this amorphous silicon thin film as an active material.
When making an amorphous silicon thin film deposit, you may supply hydrogen gas with material gas or materials powder. In this case, the amorphous silicon thin film may contain hydrogen.
When an amorphous silicon thin film contains hydrogen, the hydrogen concentration in a thin film is more than 0.001 atom %, for example. Hydrogen concentration can be measured by secondary ion mass spectrometry (SIMS).
After an example of the manufacture method according to the 1st aspect of affairs exhausts the atmospheric pressure in the sealed chamber to a high vacuum of 1Pa or less, it is the manufacture method characterized by introducing in a chamber the material gas which has SiH combination with hydrogen gas which is carrier gas, for the glow discharge excited by high frequency decomposing material gas, making an amorphous silicon thin film deposit on a substrate, and using this amorphous silicon thin film as an active material.
the -- one -- an aspect of affairs -- following -- manufacture -- a method -- others -- an example -- sealing -- having had -- a chamber -- inside -- atmospheric pressure -- one -- Pa -- less than -- a high vacuum -- having exhausted -- after -- argon -- (-- Ar --) -- gas -- said -- a chamber -- inside -- introducing -- high frequency -- exciting -- having had -- glow discharge -- it is the manufacture method which carries out sputtering of the silicon (Si) target, and is characterized by making an amorphous silicon thin film deposit on a substrate, and using this amorphous silicon thin film as an active material.
[the example of further others of the manufacture method of following the 1st aspect of affairs] After exhausting the atmospheric pressure in the sealed chamber to a high vacuum of 1Pa or less, it is the manufacture method characterized by fusing a silicon (Si) target by an electron beam, evaporating it, making an amorphous silicon thin film deposit on a substrate, and using this amorphous silicon thin film as an active material.
In each above-mentioned manufacture method, a substrate may be a heated substrate.
Moreover, in the manufacture method of the invention, before making an amorphous silicon thin film deposit on a substrate, you may perform the pretreatment by plasma irradiation or ion irradiation to the substrate surface. Such a pretreatment can raise the adhesion nature of a substrate and a silicon thin film.

As plasma irradiation, hydrogen plasma irradiation or argon plasma irradiation is mentioned for example. As ion irradiation, hydrogen ion irradiation or argon ion irradiation is mentioned, for example.

The electrode material of this invention can be used as the *** material for lithium batteries, especially a *** material for lithium secondary batteries.

As for a substrate in this invention, it is desirable that it is a current collection object. Moreover, after forming the intermediate layer for raising adhesion nature on a current collection object in this case, you may form an amorphous silicon thin film on this intermediate layer.

The 2nd aspect of affairs of this invention is the manufacture method of the electrode for lithium batteries characterized by making the active material thin film which consists of lithium and an active material to alloy deposit on a current collection object using the method of supplying materials from the gaseous phase and forming a thin film.

As a method of making an active material thin film depositing, a CVD method, the sputtering method, a thermal-spraying method, or a vacuum deposition method is mentioned.

An active material thin film consists of at least one sort of material chosen from the oxide and sulfide of a transition metal element of the element of the periodic law table IIB fellows who form lithium, a compound, or a solid solution, IIIB fellows, IVB fellows, and VB fellows and the periodic law table 4 cycle, five cycles, and six cycles, for example.

As an element of the periodic law table IIB fellows who form lithium, a compound, or a solid solution, IIIB fellows, IVB fellows, and VB fellows in this invention Carbon, aluminum, silicon, a phosphorus, zinc, gallium, germanium, arsenic, cadmium, indium, tin, antimony, mercury, thallium, a lead, and bismuth are mentioned. [moreover, the transition metal of the periodic law table 4 cycle, five cycles, and six cycles] Specifically SUKANJIUMU, titanium, vanadium, chromium, manganese, iron, Cobalt, nickel, copper, zinc, yttrium, JIRUKONIUMU. They are niobium, molybdenum, TEKUNECHIUMU, RUTENIUMU, rhodium, palladium, silver, cadmium, a rare TANOIDO system element, hafnium, tantalum, tungsten, RENIUMU, osmium, iridium, platinum, gold, and mercury.

It is desirable that it is at least one sort chosen from carbon, silicon, germanium, tin, a lead, aluminum, indium, zinc, cadmium, bismuth, and mercury also especially in the above-mentioned element, and silicon or germanium is desirable also especially in these.

As for the active material thin film in the 2nd aspect of affairs, it is desirable that it is an amorphous thin film. As an example of a desirable amorphous thin film, an amorphous silicon thin film, a micro crystallite silicon thin film, An amorphous silicon thin film, an amorphous germanium thin film, a micro crystalline germanium thin film, an amorphous germanium thin film, an amorphous silicon germanium alloy thin film, a micro crystalline silicon germanium alloy thin film, and an amorphous silicon germanium alloy thin film are mentioned.

Also in the 2nd aspect of affairs, before making an active material thin film deposit on a current collection object, you may perform the pretreatment by plasma irradiation or ion irradiation to a current collection body surface. As plasma irradiation, hydrogen plasma irradiation or argon plasma irradiation is mentioned, and hydrogen ion irradiation or argon ion irradiation is mentioned as ion irradiation.

Moreover, the active material thin film in the 2nd aspect of affairs may have the inclination structure of composition in the thickness direction.

The above-mentioned inclination structure may be formed simultaneously with deposition of an active material thin film.

As an example of the above-mentioned inclination structure, you may be the inclination structure by change of the content of the current collection object ingredient diffused in the active material thin film. When a current collection object ingredient is spread in an active material thin film, specifically, you may have the inclination structure where the concentration of a current collection object ingredient becomes low as the concentration of a current collection object ingredient is high and the surface of an active material thin film is approached near the current collection object. By forming the diffusion field of the current collection object ingredient which has such inclination structure, the adhesion nature of the active material thin film to a current collection object can be raised. In this case, when the current collection object ingredients diffused in the active material thin film are lithium and a metal ingredient which is not alloyed, the expansion and contraction of an active material thin film at the time of carrying out occlusion discharge of the lithium become small relatively. For this reason, since the stress accompanying expansion and contraction of an active material thin film becomes small near the interface with a current collection object, the exfoliation from the current collection object of the active material thin film by expansion and contraction of volume can be prevented.

Moreover, also in the 2nd aspect of affairs, after forming the intermediate layer for raising adhesion nature on a current collection object, you may form an active material thin film on this intermediate layer.

You may use the method of supplying materials from the gaseous phase and forming a thin film as a method of forming an intermediate layer. Specifically, you may form an intermediate layer by the CVD method, the sputtering method, the thermal-spraying method, or a vacuum deposition method.

Moreover, the inclination structure of composition in the above-mentioned active material thin film may be the inclination structure formed when an intermediate layer's ingredient was spread in an active material thin film.

As a current collection object in this invention, the current collection object formed from copper, iron, nickel, stainless steel, molybdenum, tungsten, tantalum, or carbon can be used, for example.

Although the thickness in particular of the current collection object in this invention is not restricted, it is desirable that it is desirable 20 more micrometers or less that it is 50 micrometers or less.
It is desirable that detailed unevenness is formed in the surface of the current collection object in this invention. Specifically, it is desirable that the surface coarseness Ra of a current collection object is 0.01-1 micrometer. The surface coarseness Ra of the current collection object is provided in Japanese Industrial Standards (JISB 0601-1994), for example, can be measured with a surface coarseness meter.
The electrodes according to the 2nd aspect of affairs are also *** for lithium batteries, and the thing which can be especially used as *** for lithium secondary batteries.
The 3rd aspect of affairs of this invention is the manufacture method of the electrode material for lithium batteries characterized by consisting of substantially a crystalline region and an amorphous field which consists of the crystalline region, a material of the same kind, or a different material, and making occlusion and the thin film to emit deposit lithium on a substrate, and using the thin film as an active material.
One of the concrete manufacture methods of the 3rd aspect of affairs supplies the materials powder containing the material gas or the composition atom of a thin film which contains the composition atom of a thin film from the gaseous phase, it makes a thin film deposit on a substrate, and is characterized by using this thin film as an active material.
Hydrogen gas may be supplied with material gas or materials powder, and a thin film may be made to deposit also in the 3rd aspect of affairs.
The deposition method of a thin film can use the same method as the 1st aspect of affairs and the 2nd aspect of affairs.
In the 3rd aspect of affairs, it is desirable that the amorphous field arranges around a crystalline region. Moreover, as for a crystalline region, it is desirable to consist of minute crystal grains.
In the thin film of the 3rd aspect of affairs, a crystalline region and/or an amorphous field may consist of the same material as the 2nd aspect of affairs of the above. Moreover, also in the 3rd aspect of affairs, like the 1st aspect of affairs and the 2nd aspect of affairs, you may prevent, before making a thin film deposit on a substrate.
The same thing as the current collection object in the 2nd aspect of affairs can be used for the current collection object in the 3rd aspect of affairs.
Moreover, also in the 3rd aspect of affairs, after forming the intermediate layer for raising adhesion nature on a current collection object like the 1st aspect of affairs and the 2nd aspect of affairs, you may form a thin film on this intermediate layer.
The manufacture method of the lithium battery of this invention is characterized by manufacturing a lithium battery, using the electrode material of the electrode manufactured on

the 1st aspect of affairs of the above, the 2nd aspect of affairs, or the 3rd aspect of affairs as "** material or ***".

The manufacture method of the lithium secondary battery of this invention is characterized by manufacturing a lithium secondary battery, using the electrode material or the electrode manufactured in the 1st aspect of affairs of the above, the 2nd aspect of affairs, or the 3rd aspect of affairs as "** material or ***".

In this invention, the still more desirable range of the surface coarseness Ra of a current collection object and a substrate is 0.05-0.5 micrometer. Impurities may be doped by active material thin films, such as the electrode active material in this invention, i.e., an amorphous silicon thin film etc. As such impurities, the element of periodic law table IIIB fellows, such as a phosphorus, aluminum, arsenic, antimony, boron, gallium, and indium, IVB fellows, and VB fellows can be mentioned, for example.

Moreover, the active material thin film in this invention laminates two or more layers, and may be formed. In the laminated each layer, composition, crystallinity, and impurities concentration may differ from hydrogen concentration etc. Moreover, you may have inclination structure in the thickness direction of a thin film as mentioned above. For example, composition, crystallinity, impurities concentration, hydrogen concentration, etc. can be made into the inclination structure where it was made to change in the thickness direction.

Moreover, although the thickness in particular of the active material thin film of this invention is not limited, it can be made into a thickness of 20 micrometers or less, for example. Moreover, in order to obtain high charge-and-discharge capacity, as for thickness, it is desirable that it is 1 micrometers or more.

In this invention, as mentioned above, in order to raise the adhesion nature of a current collection object or a substrate, and a thin film, you may prepare an intermediate layer between a current collection object or a substrate, and a thin film. As such an intermediate layer's material, a substance which forms an alloy between current collection object material or substrate material, and active material material is used preferably.

In this invention, the words of the "lithium battery" contain the lithium primary battery and the lithium secondary battery. Therefore, the electrode active material of this invention can be used as the object for lithium primary batteries, and an object for lithium secondary batteries.

[the solvent of the electrolyte used for the lithium secondary battery of this invention] Although not limited in particular, the mixed solvent of annular carbonate, such as ethylene carbonate, propylene carbonate, and butylene carbonate, and chain-like carbonate, such as dimethyl carbonate, methylethyl carbonate, and diethyl carbonate, is illustrated. Moreover, a mixed solvent with chain-like ester, such as ether system solvents, such as said annular carbonate, 1 and 2-dimethoxyethane, 1, and 2-diethoxy ethane, and gamma-butyrolactone, a sulfolane, acetic acid METCHIRU, etc. is also illustrated. As electrolytic ***, moreover, LiPF6, LiBF4,

$LiCF_3SO_3$, $LiN(CF_3SO_2)_2$, $LiN(C_2F_5SO_2)_2$, $LiN(CF_3SO_2)(C_4F_9SO_2)$, Those mixtures, such as $LiC(CF_3SO_2)_3$, $LiC(C_2F_5SO_2)_3$, $LiAsF_6$, $LiClO_4$, $Li_2B_{10}Cl_{10}$, and $Li_2B_{12}Cl_{12}$, are illustrated. Furthermore, as an electrolyte, inorganic solid electrolytes, such as the gel-like polymer electrolyte which sank the electrolysis solution into polymer electrolytes, such as polyethylene oxide, polyacrylonitrile, and polyvinylidene fluoride, and LiI, Li_3N, are illustrated. The electrolyte of the lithium secondary battery of this invention can be used without restrictions, unless Li compound as a solvent which makes ion conductivity discover, and the solvent which dissolves and holds this decompose on the voltage at the time of charge of a battery, electric discharge, or preservation.

As the quality of cathode active material of the lithium secondary battery of this invention, Lithium content transition metal oxides, such as $LiCoO_2$, $LiNiO_2$, $LiMn_2O_4$, $LiMnO_2$, $LiCo_{0.5}Ni_{0.5}O_2$, and $LiNi_{0.7}Co_{0.2}Mn_{0.1}O_2$, and the metal oxide which does not contain lithium, such as MnO_2, are illustrated. Moreover, in addition to this, if it is the substance electrochemically inserted and desorbed from lithium, it can use without restriction.

It is thought that alkaline-earth metals, such as alkaline metals, such as sodium other than lithium and potassium, magnesium, and calcium, can be used for the electrode active material of this invention also as an electrode active material of the nonaqueous electrolyte battery which uses occlusion and the electrode active material to emit, and a nonaqueous electrolyte rechargeable battery.

The best form for inventing Although this invention is hereafter explained still in detail based on a work example, in the range which is not limited to the following work example at all, and does not change the summary, it changes suitably and this invention can be carried out.

(Experiment 1)

[Production of ***]

The micro crystalline silicon thin film was formed on copper foil with the CVD method, using hydrogen gas as carrier gas, using Silang (SiH_4) as material gas, using rolling copper foil (18 micrometers in thickness) as a substrate. Copper foil as a substrate was installed on the heater in a reaction room, and, specifically, the pressure in a reaction room was exhausted to 1Pa or less with the vacuum exhaust. Then, the hydrogen (H_2) gas which is Silang (SiH_4) and carrier gas which are material gas was introduced from the material gas introduction port, and the substrate was heated to 180 degrees C at the heater. With the vacuum exhaust, the degree of vacuum was adjusted so that it might become reaction pressure, high frequency was excited with the high frequency power supply, the high frequency was introduced from the electrode, and glow discharge was induced. Detailed thin film formation conditions are shown in Table 1. In addition, the unit sccm of the flux in Table 1 is a volume flow rate per for min) per for [of 0 degree C and 1 atmosphere (101.33kPa)] 1 minute, and is Standard Cubic Centimeters Per It is the abbreviation for Minute.

表1

	成 膜 時
原料ガス（SiH_4）流量	1 0 s c c m
キャリアガス（H_2）流量	2 0 0 s c c m
基板温度	1 8 0 ℃
反応圧力	4 0 P a
高周波電力	5 5 5 W

It was made to deposit on the above-mentioned conditions until the film thickness of a micro crystallite silicon thin film was set to about 10 micrometers. The obtained thin film was a silicon thin film which consists of micro crystallite silicon included in an amorphous category. When this thin film was observed by the electron microscope, it was checked that the amorphous field arranges around the crystalline region which consists of a minute crystal grain. The obtained sample was pierced so that it might be set to 17mm in diameter, and the electrode a1 was obtained.
Next, it was made to deposit on rolling copper foil like the above until film thickness was set to about 10 micrometers in a micro crystallite silicon thin film by the sputtering method on the thin film formation conditions shown in Table 2. The obtained sample was pierced like the above and the electrode a2 was obtained.

表2

	成 膜 時
スパッタガス（Ar）流量	5 0 s c c m
キャリアガス（H_2）流量	2 0 0 s c c m
基板温度	2 0 0 ℃
反応圧力	1 0 P a
高周波電力	8 0 0 W

Next, it was made to deposit on the thin film formation conditions shown in Table 3 until film thickness was set to about 10 micrometers in a micro crystallite silicon thin film on rolling copper foil like the above by a thermal-spraying method. The obtained sample was pierced like the above and the electrode a3 was obtained. In addition, in Table 3, Unit slm is a volume flow (a part for /1000cm3) A part for part 1/1 / for /) in 0 degree C and 1 atmosphere (101.33kPa), and it is Standard Liter Per The initial of Minute is taken.

表3

	試験例
原料Siパウダー	粒径5μm
キャリアガス(Ar)流量	10slm
キャリアガス(H_2)流量	20slm
基板温度	室温
反応圧力	8×10^4Pa
高周波電力	10kW

Next, it was made to deposit until film thickness was set to about 10 micrometers in a micro crystalline silicon thin film on rolling copper foil like the above by a vacuum deposition method. The thin film formation conditions of the vacuum deposition method were vapor-deposited by electron beam (EB) vapor deposition at 1nm (10A(second))/second in having gas introduction.nothing and no substrate temperature.heating (about 40 degrees C.) and vapor deposition speed. The obtained sample was piercied like the above and the electrode a4 was obtained.

Moreover, for comparison, it mixed so that 90 weight parts and the poly tetrafluoro ethylene as a binder might serve as 10 weight parts, and commercial single-crystal-silicon powder (10 micrometers of diameters of a particle) pressed this by the metallic mold 17mm in diameter, carried out pressurization fabrication, and the electrode b1 of the pellet type was obtained.

[Production of a plus terminal]

Using Li2CO3 and CoCO3 as a starting material, weighing was carried out and it mixed by the mortar so that the atomic ratio of Li:Co might be set to 1:1, this was pressed by the metallic mold 17mm in diameter, after carrying out pressurization fabrication, it calcinated at 800 degrees C in the air for 24 hours, and the calcination object of LiCoO2 was acquired. This was ground until it became 20 micrometers of mean particle sizes by the mortar.

Acetylene black as 80 weight parts and electric conduction material was mixed so that 10 weight parts and the poly tetrafluoro ethylene as a binder might serve as 10 weight parts, and it pressed and carried out pressurization fabrication by the metallic mold 17mm in diameter, and LiCoO2 obtained powder produced the plus terminal of the pellet type.

[Production of an electrolysis solution]

LiPF6 [1mol/l] were dissolved in the constant volume mixed solvent of ethylene carbonate and diethyl carbonate, the electrolysis solution was produced to it, and this was used for it in production of the following batteries.

[Production of a battery]

The flat form lithium secondary battery was produced using the above-mentioned plus terminal and the electrolysis solution, using the above-mentioned electrode a1, a2, a3, a4, and b1 as ***.

Drawing 1 is the cross section of the produced lithium secondary battery, and consists of a plus terminal 1, **** 2, a separator 3, the plus terminal can 4, ***** 5, the plus terminal current collection object 6, a **** current collection object 7, insulating packing 8 made from polypropylene, etc.

A plus terminal 1 and **** 2 have countered through a separator 3. These are stored in the battery case which the plus terminal can 4 and ***** 5 form. A plus terminal 1 is connected to the plus terminal can 4 through the plus terminal current collection object 6, it connects with ***** 5 through the **** current collection object 7, and **** 2 has structure in which the charge and electric discharge as a rechargeable battery are possible.

The thing using the electrode a1 as **** was used as the battery A1, the thing using the electrode a2 as **** was used as the battery A2, the thing using the electrode a3 as **** was used as the battery A3, the thing using the electrode a4 as **** was used as the battery A4, and the thing using the electrode b1 as **** was used as the battery B1.

[Measurement of the charge-and-discharge cycle length characteristic]

It discharged, after charging until **** capacity became 2000 mAh/g with the current value A of 100micro in 25 degrees C, and this was made into the charge and discharge of 1 cycle, and the capacity maintenance rate of 50 cycle eye was measured about each battery. In addition, about the battery B1 which was not charged to 2000 mAh/g, it charged to 4.2V, it discharged after that, and the cycle examination was done. A result is shown in Table 4.

表4

電池	負極活物質	50サイクル目の容量維持率
A1	CVD法作製微結晶シリコン	85%
A2	スパッタ法作製微結晶シリコン	78%
A3	溶射法作製微結晶シリコン	43%
A4	真空蒸着法作製微結晶シリコン	60%
B1	シリコン粉末	5%

The battery A1 manufactured according to this invention, A2, A3, and A4 show the remarkable high capacity maintenance rate compared with the comparative battery B1 so that clearly from the result shown in Table 4.

Moreover, as a result of measuring diffusion of the copper atom to the inside of the silicon thin

film in a battery A1 and the electrode used by A2 by SIMS, about 1 micrometer of things which the copper atom has diffused by the concentration of about several percent also in the inside of the thin film which got used were checked from the interface.
As mentioned above, the charge-discharge cycle characteristic of the lithium secondary battery is remarkably improved by using the micro crystallite silicon thin film which might be followed by the manufacture method of this invention as a *** active material. although it is not clear for details about this Reason, in order that the amorphous field in a micro crystallite silicon thin film may ease occlusion and the expansion contraction at the time of emitting for lithium -- a *** active material -- fine -- powdering can be controlled and the high adhesion nature by inclination structure is further conjectured to have controlled aggravation of the current collection characteristic.
(Experiment 2)
Before forming a micro crystallite silicon thin film, the pretreatment by plasma irradiation or ion irradiation was performed to the substrate surface, i.e., the copper foil surface, and the effect of the pretreatment was examined. In addition, the rolling copper foil same with having used in the experiment 1 as a substrate was used.
[A pretreatment by plasma irradiation]
Like the cases of production of the electrode a1 of experiment 1, copper foil as a substrate was installed on the heater in a reaction room, and the pressure in a reaction room was exhausted to 1Pa or less with the vacuum exhaust. Next, hydrogen (H2) gas was introduced into the reaction interior of a room so that it might be set to 200sccm, the substrate was heated to 180 degrees C of the heater, hydrogen plasma was generated on condition of the high frequency electric power 555W, and this was irradiated for 10 minutes at copper foil. Then, it was made to deposit like the electrode a1 of experiment 1 until film thickness was set to about 10 micrometers in a micro crystallite silicon thin film with a CVD method. The obtained sample was pierced like the above-mentioned experiment 1, and the electrode a5 was obtained.
[A pretreatment by ion irradiation]
In the same reaction interior of a room as the pretreatment by the above-mentioned plasma irradiation, argon (Ar) gas as introductory gas 200sccm, And by introducing hydrogen (H2) gas into the reaction interior of a room by the flux of 200sccm, preparing a high frequency power supply apart from the high frequency power supply for generating plasma, and impressing high frequency electric power to a substrate from this power supply By making a substrate generate bias voltage-80V and generating plasma on condition of the substrate temperature of 180 degrees C, and the high frequency electric power 555W, ion was irradiated to copper foil and it pretreated for 10 minutes. Then, the micro crystallite silicon thin film was made to deposit with a CVD method like the electrode a1 of experiment 1 until film thickness was set to about 10 micrometers. The obtained sample was pierced like the experiment 1 and the electrode a6 was

obtained.
The experiment which evaluates adhesion nature about the obtained electrode a5, an electrode a6, and the electrode a1 in the above-mentioned experiment 1 was conducted. Using the Vickers pressure child pushing testing machine, 1kg of load was applied to the micro crystallite silicon thin film, the number which exfoliation generated in 100 totals was measured, and the rate of incidence of exfoliation was searched for. A result is shown in Table 5. Moreover, using electrodes a5 and a6, batteries A5 and A6 were produced like the above-mentioned experiment 1, and the charge-and-discharge cycle length characteristic was evaluated like the experiment 1 about this. An evaluation result is shown in Table 5. In addition, in Table 5, the result of the battery A1 is shown collectively.

表 5

電池（電極）	前処理	密着性（剥離発生率）	50サイクル目の容量維持率
A5（a5）	プラズマ処理	7%	91%
A6（a6）	イオン照射	6%	92%
A1（a1）	無し	24%	85%

In the electrode which performed the pretreatment by plasma polymerization or ion processing, the adhesion nature to copper foil of a silicon thin film is good so that clearly from the result shown in Table 5. Moreover, compared with the battery A1 using the electrode a1 which is not pretreating, the charge-discharge cycle characteristic of the batteries A5 and A6 using the electrodes a5 and a6 which pretreated is improving. The adhesion nature of this to copper foil of a silicon thin film improves, and since the exfoliation from copper foil of the *** active material at the time of being charge and discharge was controlled further, it is guessed.
In addition, in the above-mentioned experiment, although rolling copper foil is used as copper foil, it is checking that the effect of the pretreatment with the same said of electrolysis copper foil which is large copper foil of the surface coarseness Ra is acquired.
Industrial availability According to this invention, charge-and-discharge capacity is high, and the electrode material which can be used as the lithium secondary battery excellent in the charge-discharge cycle characteristic can be manufactured.
[Brief Description of the Drawings]
Drawing 1 is the cross section showing the lithium secondary battery produced in the work example of this invention.

[Translation done.]